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(71) Applicant: WITCO CORPORATION [US/US]; One American Lane, Greenwich, CT 06831-2559 (US).

(72) Inventors: MANNING, Monna, Marie; 654 Wilson Avenue, Columbus, OH 43205 (US). ALLARDICE, Andrea, Susan; 4778 Hayden Boulevard, Columbus, OH 43221 (US). FRIEDLI, Floyd; 9406 Avemore Court, Dublin, OH 43107 (US).

(74) Agents: BLACK, Donald, T. et al.; Scully, Scott, Murphy &amp; Presser, 400 Garden City Plaza, Garden City, NY 11530 (US).

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(54) Title: BIODEGRADABLE QUATERNARY HAIR AND SKIN CONDITIONERS

(57) Abstract

Disclosed are conditioning compositions for the hair and skin containing compounds of the formula  $(R^1)(R^2)N(CH_2CH_2OC(O)R)_2X^-$ ; wherein  $R^1$  is alkyl containing 1 to 6 carbon atoms, or hydroxyalkyl containing 1 to 6 carbon atoms;  $R^2$  is alkyl containing 1 to 6 carbon atoms, or benzyl;  $X^-$  is an anion; and R is alkyl and alkylene of 12 to 22 carbon atoms having 0 to 3 carbon-carbon double bonds, provided that at least 2 different chain lengths R are present and 0, 1 and 2 such double bonds are present.

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1     BIODEGRADABLE QUATERNARY HAIR AND SKIN CONDITIONERS

BACKGROUND OF THE INVENTION

5     The present invention relates to conditioning hair and skin, particularly the hair and skin of the human body. More particularly, the present invention relates to methods of imparting conditioning to the hair and skin and to compositions useful as hair conditioners and skin conditioners.

10     Hair conditioning imparts to the hair many attributes which are perceivable and are considered to be desirable. That is, hair conditioners are used so that the hair feels, to the touch, smoother and softer. In addition, hair conditioners are used to render the  
15 hair more easily rinsable when it is washed or rinsed, to improve the wet and dry combability of the hair, and to impart to the hair greater ease of detangling and greater manageability to combing, brushing and styling.

      Skin conditioners are used generally to  
20 improve the feel of the skin to the touch, rendering the skin softer and smoother feeling. In addition, skin conditioners are used to impart to the skin a feeling of fullness and smoothness as well as freedom from dryness and freedom from roughness.

25     Numerous compositions have been available commercially for conditioning the hair and the skin. More recently, however, governmental regulations and the preferences of the individual consumer have given rise to concerns that consumer products including hair  
30 conditioners and skin conditioners not pose excessive risks of damage to the environment. While these

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1 concerns have generally been addressed by improvements  
in composition so that materials when discarded or  
washed away are relatively less damaging to the  
environment, it would be useful to be able to formulate  
5 hair conditioning products and skin conditioning  
products which are in fact biodegradable. In this way,  
the desirable conditioning properties would be provided,  
and the product upon disposal or removal by washing and  
the like would be capable of biodegrading, that is,  
10 being converted by the processes normally encountered in  
waste water treatment and the like into components which  
pose an even lesser risk of harm to the environment and  
which can be dealt with ever more easily by the  
customary processes for treating solid waste and waste  
15 water.

Unfortunately, actual experience prior to the  
present invention has generally found that agents that  
might be considered in hair conditioning compositions  
and skin conditioning compositions, which agents are  
20 found to be biodegradable, perform only poorly if at all  
as conditioning agents for the hair and skin. In fact,  
this experience has been encountered so uniformly that  
there has seemed to be essentially a negative  
correlation between biodegradability and effectiveness  
25 as a conditioner for the hair and skin; that is, an  
agent found to be biodegradable would accordingly not be  
expected to, and would not, perform adequately as a  
conditioning agent for the hair and skin.

Thus, there remains a need for conditioning  
30 agents and for compositions containing such agents  
exhibiting biodegradability and also exhibiting

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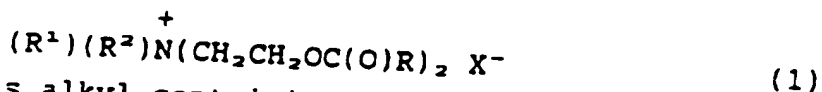
1 exemplary performance as conditioners for the hair and  
 skin. The present invention satisfies this need, even  
 in the face of expectations to the contrary as drawn  
 from experience with many biodegradable compounds.

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### BRIEF SUMMARY OF THE INVENTION

One aspect of the present invention is a  
 method for conditioning hair comprising applying to the  
 hair a conditioning effective amount of a composition  
 10 comprising

(a) from 0.1 wt.% to 10 wt.% of a mixture of  
 compounds of the formula (1)



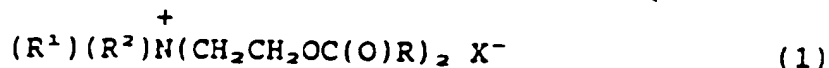
15 wherein  $R^1$  is alkyl containing 1 to 6 carbon atoms, or  
 hydroxyalkyl containing 1 to 6 carbon atoms;  $R^2$  is alkyl  
 containing 1 to 6 carbon atoms, or benzyl;  $X^-$  is an  
 anion; and R is selected from the group consisting of  
 alkyl and alkylene groups containing 11 to 23 carbon  
 20 atoms and up to 3 carbon-carbon double bonds, provided  
 that said mixture contains compounds of formula (1)  
 containing R groups which have at least 2 different  
 chain lengths and containing R groups which have 0, 1  
 and 2 carbon-carbon double bonds; and

25 (b) a vehicle which imparts to said  
 composition fluidity upon application thereof to the  
 hair and which has a pH value compatible with said hair.

Another aspect of the present invention is a  
 method for conditioning skin comprising applying to the  
 30 skin a conditioning effective amount of a composition  
 comprising

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- 1 (a) from 0.1 wt.% to 10 wt.% of a mixture of  
compounds of the formula (1)

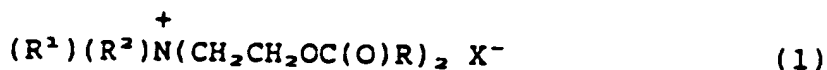


- 5 wherein  $R^1$  is alkyl containing 1 to 6 carbon atoms, or  
hydroxyalkyl containing 1 to 6 carbon atoms;  $R^2$  is alkyl  
containing 1 to 6 carbon atoms, or benzyl;  $X^-$  is an  
anion; and R is selected from the group consisting of  
10 alkyl and alkylene groups containing 11 to 23 carbon  
atoms and up to 3 carbon-carbon double bonds, provided  
that said mixture contains compounds of formula (1)  
containing R groups which have at least 2 different  
chain lengths and containing R groups which have 0, 1  
and 2 carbon-carbon double bonds; and

- 15 (b) a vehicle which imparts to said  
composition fluidity upon application thereof to the  
skin and which has a pH value compatible with said skin.

Another aspect of the present invention is  
compositions useful for conditioning hair, comprising

- 20 a) from 0.1 wt.% to 10 wt.% of a mixture of  
compounds of the formula (1)



- wherein  $R^1$  is alkyl containing 1 to 6 carbon atoms, or  
hydroxyalkyl containing 1 to 6 carbon atoms;  $R^2$  is alkyl  
25 containing 1 to 6 carbon atoms, or benzyl;  $X^-$  is an  
anion; and R is selected from the group consisting of  
alkyl and alkylene groups containing 11 to 23 carbon  
atoms and up to 3 carbon-carbon double bonds, provided  
that said mixture contains compounds of formula (1)  
30 containing R groups which have at least 2 different

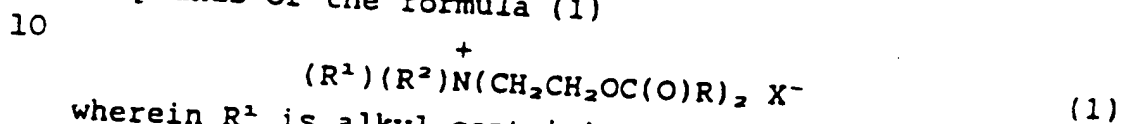
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1 chain lengths and containing R groups which have 0, 1  
and 2 carbon-carbon double bonds; and

(b) a vehicle which imparts to said  
composition fluidity upon application thereof to the  
5 hair and which has a pH value compatible with said hair.

Yet another aspect of the present invention is  
compositions useful for conditioning skin, comprising

(a) from 0.1 wt.% to 10 wt.% of a mixture of  
compounds of the formula (1)



wherein  $R^1$  is alkyl containing 1 to 6 carbon atoms, or  
hydroxyalkyl containing 1 to 6 carbon atoms;  $R^2$  is alkyl  
containing 1 to 6 carbon atoms, or benzyl;  $X^-$  is an  
15 anion; and R is selected from the group consisting of  
alkyl and alkylene groups containing 11 to 23 carbon  
atoms and up to 3 carbon-carbon double bonds, provided  
that said mixture contains compounds of formula (1)  
containing R groups which have at least 2 different  
20 chain lengths and containing R groups which have 0, 1  
and 2 carbon-carbon double bonds; and

(b) a vehicle which imparts to said  
composition fluidity upon application thereof to the  
skin and which has a pH value compatible with said skin.

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#### DETAILED DESCRIPTION OF THE INVENTION

The compounds of formula (1) having any single  
chain length R and any given degree of saturation or  
unsaturation are known, individually, per se.

30

The desired mixture of compounds in accordance  
with this invention having compounds of several  
different chain lengths R and degrees of saturation and

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1 unsaturation can be synthesized by a series of reactions  
carried out under conditions familiar to those of  
ordinary skill in this art. For instance, a methyl-  
bis(2-hydroxyethyl) tertiary amine can be reacted with  
5 an appropriate blend of fatty acids of the general  
formula  $RC(O)OH$  as defined furthermore herein, the  
reaction being carried out under esterifying conditions  
with a sufficient amount of such fatty acids to provide  
complete esterification of both hydroxyl groups on the  
10 tertiary amine. Thereafter, the diesterified tertiary  
amine is reacted with a quaternizing reagent of the  
formula  $CH_3X$ , such as methylchloride or dimethylsulfate,  
in order to provide a second methyl group onto the  
nitrogen atom, thereby forming the desired quaternary  
15 ammonium compound.

The substituents  $R^1$  and  $R^2$  defined hereinabove  
are preferably both methyl, or both ethyl, or one is  
methyl or ethyl and the other is benzyl or hydroxyalkyl,  
preferably hydroxyethyl or hydroxymethyl.

20 In formula (1) as defined herein, the anion  $X^-$   
counterbalances the positive charge of the quaternary  
ammonium compound. Thus, the quaternizing compound has  
the formula  $CH_3X$ . The anion  $X$  is preferably any anion  
forming the desired compound capable of quaternizing the  
25 tertiary amines so as to form the desired dimethyl-  
substituted quaternary ammonium compound. Preferred  
examples of  $X^-$  include chloride, bromide and  
methylsulfate.

Referring again to formula (1), the  
30 substituent  $R$  is selected from the group consisting of  
alkyl and alkylene groups containing 12 to 24 carbon



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1 atoms and 0, 1, 2 or 3 carbon-carbon double bonds. It  
has been determined that superior conditioning  
properties are exhibited by compounds corresponding to  
the above formula (1) provided that the compounds  
5 corresponding to that formula (1) which are present in  
the conditioning composition represent a mixture of  
chain lengths of the substituent R and also represent a  
mixture of saturated and mono-unsaturated and di-  
unsaturated chains. It is recognized, of course, that  
10 any one compound of formula (1) can have no more than  
two particular R groups, and that within any one  
molecule the R groups can be the same or different.  
However, the superior conditioning properties that the  
conditioning compositions of the present invention have  
15 been found to possess are provided by including in the  
compositions compounds corresponding to formula (1)  
wherein compounds are present which exhibit R groups  
containing at least five different chain lengths and  
containing R groups which have no carbon-carbon double  
20 bonds, R groups which have one carbon-carbon double  
bond, and R groups which have two carbon-carbon double  
bonds. Hair and skin conditioning compositions  
containing mixtures of compounds of formula (1) have  
been found to exhibit conditioning superior to that  
25 exhibited by conditioning agents of formula (1) wherein  
all the R groups are the same.

The requirement that the conditioning  
compositions contain compounds of formula (1) exhibiting  
a number of different chain lengths and degrees of  
30 saturation can be readily met by reacting the precursor  
bis(hydroxyl) tertiary amine with products containing a

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1 mixture of fatty acids of varying chain lengths and  
varying degrees of unsaturation. Such mixtures of acids  
are known and are commercially available as, for  
instance, tallow acids, rapeseed oil acids, palm oil  
5 acids, palm stearine acids, and canola oil acids, which  
are particularly preferred examples as used in the  
present invention. The fatty acids present in each of  
these naturally occurring products contain five or more  
different chain lengths and contain acids having no  
10 unsaturation, as well as acids which are mono-  
unsaturated, di-unsaturated and tri-unsaturated. More  
particularly, the distribution of fatty acids and their  
chain lengths and number of double bonds are set forth  
in the following table.

15           The following table describes tallow acids and  
rapeseed oil acids, which are two preferred acid  
mixtures useful in this invention. Each number  
represents a percent by weight of the entire mixture of  
acids and has a margin of  $\pm 0.2$  wt.%.  
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Fatty Acids	Carbon Atoms	Double Bonds	Tallow	Rapeseed Oil
5 Lauric	12	0	0.1	---
Myristic	14	0	3.2	0.1
Myristoleic	14	1	0.9	---
Pentadecanoic	15	0	0.5	---
Palmitic	16	0	24.3	3.8
10 Palmitoleic	16	1	3.7	0.3
Margaric	17	0	1.5	---
Margaroleic	17	1	0.8	---
Stearic	18	0	18.6	1.2
Oleic	18	1	42.6	18.5
15 Linoleic	18	2	2.6	14.5
Linolenic	18	3	0.7	11.0
Arachidonic	20	0	0.2	0.7
Gadoleic	20	1	0.3	6.6
Eicosadienoic	20	2	---	0.7
20 Behenic	22	0	---	0.5
Erucic	22	1	---	41.1
Lignoceric	24	0	---	1.0
Iodine Value Range			40-55	100-115

25

The compositions according to the present invention can be formulated with any cosmetically acceptable vehicle which is inert to the conditioning agent and to the hair or skin, as the case may be. By "cosmetically acceptable" is meant that the vehicle is

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1 inert to the skin or hair and permits easy, even  
application to the skin or hair of a thin film which  
contains the reaction product. Such vehicles can  
comprise any of a large variety of forms, including oil-  
5 in-water emulsions, water-in-oil emulsions, anhydrous  
compositions such as oil-based liquids, slurries,  
powders or pastes, and aqueous solutions, slurries and  
pastes. The conditioning compositions preferably  
contain a total of from about 0.1 wt.% to about 10 wt.%  
10 of the indicated mixture of compounds of the formula  
(1).

Compositions according to this invention can  
include water as a vehicle, usually with at least one  
other cosmetically-acceptable vehicle.

15 Vehicles other than water that can be used in  
compositions according to the invention can include  
liquids or solids as emollients, solvents, humectants,  
thickeners and powders. Examples of each of these types  
of vehicles, which can be used singly or as mixtures of  
20 one or more vehicles, are as follows:

Emollients, such as stearyl alcohol, glyceryl  
ricinoleate, glyceryl stearate, propane-1,2-diol,  
butane-1,3-diol, mink oil, cetyl alcohol,  
stearamidopropyl dimethylamine, isopropyl isostearate,  
25 stearic acid, isobutyl palmitate, isocetyl stearate,  
oleyl alcohol, isopropyl laurate, hexyl laurate, decyl  
oleate, octadecan-2-ol, isocetyl alcohol, eicosanyl  
alcohol, behenyl alcohol, cetyl palmitate, silicone oils  
such as dimethylpolysiloxane, dimethicone copolyols, di-  
30 n-butyl sebacate, isopropyl myristate, isopropyl  
palmitate, isopropyl stearate, butyl stearate,

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- 1 polyethylene glycol, triethylene glycol, lanolin, cocoa  
butter, corn oil, cotton seed oil, tallow, lard, olive  
oil, palm kernel oil, rapeseed oil, safflower seed oil,  
soybean oil, sunflower seed oil, olive oil, sesame seed  
5 oil, coconut oil, arachis oil, castor oil, acetylated  
lanolin alcohols, petrolatum, mineral oil, butyl  
myristate, isostearic acid, palmitic acid, isopropyl  
linoleate, lauryl lactate, myristyl lactate, decyl  
oleate, myristyl myristate;
- 10 Solvents such as ethyl alcohol, propylene  
glycol, water, isopropanol, castor oil, ethylene glycol  
monoethyl ether, diethylene glycol monobutyl ether,  
diethylene glycol monoethyl ether, dimethyl sulphoxide,  
dimethyl formamide, tetrahydrofuran;
- 15 Humectants, such as glycerin, sorbitol, sodium  
2-pyrrolidone-5-carboxylate, soluble collagen, dibutyl  
phtalate, propylene glycol, gelatin;
- Powders can include components such as chalk,  
talc, fullers earth, kaolin, starch, gums, colloidal  
20 silicon dioxide, sodium polyacrylate, tetra alkyl and/or  
trialkyl aryl ammonium smectites, chemically modified  
magnesium aluminum silicate, organically modified  
montmorillonite clay, hydrated aluminum silicate, fumed  
silica, carboxyvinyl polymer, cellulose such as  
25 hydroxyethyl cellulose and sodium carboxymethyl  
cellulose, ethylene glycol monostearate, zinc or  
magnesium stearate, zinc oxide and magnesium oxide.  
These components may also be used as thickeners in fluid  
or semi-fluid compositions.
- 30 Examples of additional composition types are  
found in Encyclopedia of Chemical Technology, Vol. 7,

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1 Pages 146-150 and 155-160 (John Wiley & Sons, 1979), the disclosure of which is hereby incorporated herein by reference.

Examples of other conventional adjuncts, some  
5 of which can also function as vehicles, that may optionally be employed, include volatile and non-volatile silicones; silicone polymers; preservatives, such as para-hydroxy benzoate esters; humectants, such as butane-1,3-diol, glycerol, sorbitol, polyethylene  
10 glycol; stabilizers, such as sodium chloride or ammonium chloride; buffer systems, such as lactic acid together with a base such as sodium hydroxide; oils and waxes, such as avocado oil, Evening Primrose oil, mineral oil, petrolatum, sunflower oil, beeswax, ozokerite wax,  
15 paraffin wax, lanolin, lanolin alcohol; emollients; thickeners; activity enhancers; colorants; whiteners; fragrances; and bactericides.

When the desired conditioning composition is a solution, one can simply stir together the desired  
20 amount of the mixture of compounds of formula (1) together with the solvent, such as water or, for instance, a lower alcohol containing 1-6 carbon atoms in which the mixture is soluble, or a mixture of water and such an alcoholic component. A useful embodiment is a  
25 solution of 85% active and 15% ethanol. A preferred embodiment is 75% active and 25% propylene glycol.

When it is desired that the composition is in the form of an emulsion, for instance as a cream or lotion, the composition should also contain an  
30 emulsifier component which is constituted of one or more emulsifiers chosen to provide the HLB (hydrophilic-

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- 1 lipophilic balance) appropriate to whether the aqueous  
or oil phase is the continuous phase, and appropriate to  
the choice of the particular components present.  
Suitable cosmetically acceptable emulsifiers abound and  
5 are well known to the cosmetic chemist. Examples  
include compounds having a long-chain alkyl or alkylene  
chain of 12 to 20 carbon atoms substituted with a chain  
of 4 to 20 ethoxy or propoxy units; and glycol or  
glycerol derivatives substituted with an alkyl or  
10 alkylene chain of 12 to 24 carbon atoms. Further  
examples are found in Encyclopedia of Chemical  
Technology, Vol. 8, Pages 913-916 (John Wiley & Sons,  
1979), which are hereby incorporated herein by  
reference.
- 15 The topical skin conditioner compositions of  
the invention can be formulated as a fluid, for example  
in a product such as a lotion, with or without an  
applicator such as a roll-ball applicator, or a  
container fitted with a pump to dispense the  
20 composition, for example as a cream or mousse, or simply  
in a non-deformable bottle or squeeze container.  
Alternatively, the composition of the invention may be  
semi-solid, for example as a cream, lotion, gel, paste  
or ointment for use in conjunction with a suitable  
25 applicator or simply in a tube or lidded jar. Hair and  
skin conditioner compositions are preferably flowable  
liquids (solutions, emulsions or dispersions) although  
they can be in the form of thickened gels, pastes and  
the like that can be rubbed into and onto the hair or  
30 skin.

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1           The conditioning compositions useful in the  
present invention will preferably contain in addition  
substances effective to adjust the pH of the composition  
to values within desired ranges compatible with the  
5 surface to which the conditioning agent will be applied.  
Thus, for instance, it is preferred that the pH of a  
hair conditioning composition be in the range of about  
4.0 to about 5.5 in order to provide proper  
compatibility with the hair shaft itself. It is  
10 preferred that skin conditioning compositions have a pH  
of about 3.5 to about 5.5 in order to provide proper  
conditioning to the skin while avoiding irritation that  
would ensue from pH values that are too low or too high.  
Suitable agents for adjusting the pH to within these  
15 desired limits without otherwise disturbing the desired  
attributes of the conditioning compositions include  
citric acid (to adjust the pH downwards) and small  
amounts of sodium hydroxide (to adjust the pH upwards).

          The conditioning compositions can also contain  
20 additional adjuvants which enhance the conditioning  
properties of the compositions and agents which provide  
fluidity to the composition. As is familiar to those  
having experience in this field, the conditioning  
compositions are preferably flowable liquids which  
25 retain sufficient viscosity that they do not immediately  
run off of the surface to which they are applied.

          Thus, it is preferred that the conditioning  
compositions include one or more fatty alcohols, by  
which is meant compositions of the formula  $R^1OH$  wherein  
30  $R^1$  represents an alkyl or alkylene group, straight or



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1 branched, containing 12-22 carbon atoms and 0, 1 or 2  
carbon-carbon double bonds.

The formulation of the compositions is  
straightforward and well within the skill of those  
5 familiar with the manufacture of conditioning  
compositions. The ingredients are stirred together in a  
suitable mixing vessel until a homogeneous flowable  
composition is formed. The composition is then metered  
into appropriate containers, sealed and available for  
10 shipment to the point of purchase.

The resulting conditioning compositions can be  
used in the manner presently employed with conventional  
hair conditioning compositions and skin conditioning  
compositions. For use on the hair, it is adequate to  
15 pour an amount generally ranging from about 1 to about 5  
grams onto the hair, to work it into the hair  
thoroughly, and then to rinse it from the hair. For  
skin conditioning compositions, amounts generally used  
are on the order of 0.5 to 2 fluid ounces which are  
20 applied to the skin or applied to the hands and then  
rubbed onto the skin with any excess amounts of  
conditioner simply wiped off of the skin. It will be  
recognized that the appropriate amount to use can  
readily be ascertained as a function of the conditioning  
25 effect imparted by the composition and as a function of  
the volume of hair or area of skin that is desired to be  
conditioned.

The present invention will be further  
illustrated in the following examples, which are  
30 included for purposes of illustration and are not  
intended to be limiting.

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EXAMPLE 1

This example compares compositions in accordance with the present invention with other formulations for properties as a hair conditioner.

5

The formulations that were tested were:

Formulation 1-1

	<u>Ingredient</u>	<u>Wt. %</u>
10	Quaternium-18 (dimethyldihydrogenated tallow ammonium chloride), 68% active in propylene glycol ("Varisoft 432 PPG," Witco Chemical Co.)	1.47
	Cetyl Alcohol ( $\text{CH}_3(\text{CH}_2)_{15}\text{OH}$ )	2.0
15	Ceteareth-20 (having the formula $\text{R}(\text{OCH}_2\text{CH}_2)_n\text{OH}$ wherein R is a mixture of cetyl and stearyl and n has an average value of 20)	1.0
	Citric acid, as 25 wt. % solution in water	to pH 4.0-4.4
20	DI (deionized) Water	95.53

Formulation 1-2

	<u>Ingredient</u>	<u>Wt. %</u>
25	PPG-9 Dimethylmonium chloride (Methyl-diethyl-poly(propoxy)- ammonium chloride having an average of 9 propoxy units) 95% active in water ("Emcol CC-9," Witco Chemical Co.)	1.05
	Cetyl Alcohol	2.0
	Ceteareth-20	1.0
30	Citric acid, as 25 wt. % solution in water	to pH 4.0-4.4
	DI Water	95.95

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1 Formulation 1-3

<u>Ingredient</u>		<u>Wt. %</u>
5	PPG-40 Diethylmonium chloride (Methyl-diethyl-poly(propoxy)- ammonium chloride having an average of 40 propoxy units) ("Emcol CC-42," Witco Chemical Co.)	1.05
	Cetyl Alcohol	2.0
	Ceteareth-20	1.0
	Citric acid, as 25 wt. % solution in water	to pH 4.0-4.4
10	DI Water	95.95

Formulation 1-4

<u>Ingredient</u>		<u>Wt. %</u>
15	Steapyrium chloride (1-(2-hydroxyethyl) carbamoyl methyl pyridinium chloride stearate), 94% active ("Emcol E-607S," Witco Chemical Co.)	1.06
	Cetyl Alcohol	2.0
	Ceteareth-20	1.0
20	DI Water	95.94
	Citric acid, as 25 wt. % solution in water	to pH 4.0-4.4

Formulation 1-5

<u>Ingredient</u>		<u>Wt. %</u>
25	Lapyrium chloride (1-(2-hydroxyethyl) carbamoyl methyl pyridinium chloride laurate), 97.5% active ("Emcol E-607L," Witco Chemical Co.)	1.06
	Cetyl Alcohol	2.0
	Ceteareth-20	1.0
30	DI Water	95.97
	Citric acid, as 25 wt. % solution in water	to pH 4.0-4.4

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1 Formulation 1-6

	<u>Ingredient</u>	<u>Wt. %</u>
	Mixture of compounds of formula (1), derived from 5 soft (partially hydrogenated) tallow acids, 82% actives, X = Cl	1.22
	Cetyl Alcohol	2.0
	Ceteareth-20	1.0
	DI Water	95.78
10	Citric acid, as 25 wt.% solution in water	to pH 4.0-4.4

Formulation 1-7

	<u>Ingredient</u>	<u>Wt. %</u>
15	Mixture of compounds of formula (1), derived from hydrogenated tallow acids, 82% active, X = Cl	1.22
	Cetyl Alcohol	2.0
	Ceteareth-20	1.0
	DI Water	95.78
20	Citric acid, as 25 wt.% solution in water	to pH 4.0-4.4

Each formulation was prepared as follows: the water, and separately the ingredients other than water or citric acid, were measured into separate beakers.

25 Each beaker was heated over a steam bath until the contents were at 75-80°C. The beakers were then removed from the heat, the contents were combined and stirred until cool, and citric acid as necessary was added.

A hair swatch evaluation test was then  
30 performed to assess the performance of each formulation as a hair conditioner. Hair swatches were prepared and tested as follows:

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1 Hair for the tests was certified virgin European brown hair. The hair samples were banded and glued in 5 gram tresses.

Procedure:

- 5 1. Wet hair tress with warm tap water and apply 3 cc of a 5 wt.% solution of sodium lauryl sulfate in deionized water.
2. Wash hair for 2 minutes and rinse for 1 minute under running tap water at 40°C.
- 10 3. Squeeze excess water from hair and place tress in large weighing dish.
4. Weigh 0.5 gram of a 1% active conditioner onto the hair tress.
- 15 5. Massage conditioner evenly through the hair for 2 minutes and rinse for 1 minute under running tap water at 40°C.
6. Squeeze out excess water and blot dry between layers of paper towels.
- 20 7. Comb hair and evaluate for wet comb and wet detangle.
8. Roll hair onto a 1-inch plastic roller and hang to dry overnight.
9. Remove roller and evaluate for dry characteristics including dry comb, manageability, dry detangle, bounce/body, curl, and shine.
- 25 10. Report results as a number (5 = best) and/or use descriptive words.

30 These results indicate that hair conditioning compositions in accordance with the present invention exhibit superior conditioning.

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1           The results are set forth in the following  
 Table 1:

Table 1

5

Conditioner Formulation		<u>1-1</u>	<u>1-2</u>	<u>1-3</u>	<u>1-4</u>	<u>1-5</u>	<u>1-6</u>	<u>1-7</u>
10	Feel on Hair	3.0	3.0	2.5	4.0	4.5	5.0	5.0
	Rinsability	3.5	3.0	3.5	4.0	4.5	4.5	4.5
	Wet Comb	3.5	3.0	3.0	4.0	4.5	4.5	4.5
	Detangle	3.0	3.0	2.5	3.5	4.5	4.5	4.0
15	Dry Comb	3.0	3.0	2.5	4.0	3.5	4.0	4.0
	Detang e	3.5	2.5	2.0	4.5	3.5	4.0	3.5
	Antistatic	2.5	2.5	2.0	3.5	3.0	3.5	3.5
	Bounce/Body	3.5	3.0	2.5	3.0	3.0	3.5	3.5
20	Manageability	3.0	3.0	2.5	3.5	3.0	3.5	3.5
	Shine	3.0	3.0	2.0	3.0	3.0	3.0	3.0
25	Total (Average)	3.15	2.9	2.5	3.7	3.7	4.0	3.9

          These results indicate that hair conditioning  
 compositions in accordance with the present invention  
 30 exhibit superior conditioning compound to compositions  
 based on other conditioning agents.

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EXAMPLE 2

This example compares compositions in accordance with the present invention with compositions based on agents of a single chain length R.

5

The formulations that were tested were:

Formulation 2-1

<u>Ingredient</u>		<u>Wt. %</u>
10	A compound corresponding to formula (1) except that both R groups were C <sub>13</sub> alkyl, X = Cl	1.0
	Cetyl Alcohol	2.0
	Ceteareth-20	1.0
	DI Water	96.0
15	Citric acid, as 25 wt. % solution in water	to pH 4.0-4.4

Formulation 2-2

<u>Ingredient</u>		<u>Wt. %</u>
20	A compound corresponding to formula (1) except that both R groups were C <sub>13</sub> alkyl, X = Cl	1.0
	Cetyl Alcohol	2.0
	Ceteareth-20	1.0
	DI Water	96.0
25	Citric acid, as 25 wt. % solution in water	to pH 4.0-4.4

30

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1 Formulation 2-3IngredientWt. %A compound corresponding to  
formula (1) except that

1.0

5 both R groups were C<sub>17</sub> alkyl,

X = Cl

Cetyl Alcohol

2.0

Ceteareth-20

1.0

DI Water

96.0

Citric acid, as 25 wt. %  
solution in water

to pH 4.0-4.4

10

Formulation 2-4IngredientWt. %Conditioning agent of formula  
(1) derived from hydrogenated

1.0

15 tallow acids, X = CH<sub>2</sub>SO<sub>4</sub>.

Cetyl Alcohol

2.0

Ceteareth-20

1.0

DI Water

96.0

Citric acid, as 25 wt. %  
solution in water

to pH 4.0-4.4

20

Formulation 2-5IngredientWt. %Conditioning agent as in  
Formulation 2-4 except  
that all R groups were

1.0

25 C<sub>17</sub> alkyl

Cetyl Alcohol

2.0

Ceteareth-20

1.0

DI Water

96.0

Citric acid, as 25 wt. %  
solution in water

to pH 4.0-4.4

30

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1 Formulation 2-6

<u>Ingredient</u>	<u>Wt. %</u>
Conditioning agent of formula (1) derived from rapeseed oil acids, X = Cl, (71.3% actives)	1.15
Cetyl Alcohol	2.0
Ceteareth-20	1.0
DI Water	95.85
Citric acid, as 25 wt.% solution in water	to pH 4.0-4.4

10

Each formulation was prepared by combining the first listed product and the water in one container, combining the other ingredients in a separate container, heating each container over a steam bath until the contents were at 75-80°C, removing the heat, combining the contents of the two containers, and stirring the product until cool.

Each formulation was then tested on hair following the procedure described in Example 1. The results are set forth in Table 2:

25

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-24-

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Table 2

5	Conditioner	<u>1-1</u>	<u>1-6</u>	<u>1-7</u>	<u>2-1</u>	<u>2-2</u>	<u>2-3</u>	<u>2-4</u>	<u>2-5</u>	<u>2-6</u>
	<u>Formulation</u>									
	Feel on Hair	3.0	5.0	5.0	2.7	4.9	4.9	4.9	2.6	5.0
	Rinsability	3.5	4.5	4.5	3.5	4.5	4.5	4.5	3.3	4.5
10	Wet Comb	3.2	4.5	4.5	2.9	4.6	4.5	4.5	2.5	4.6
	Detangle	3.0	4.6	4.4	2.3	4.0	4.2	4.5	2.1	4.6
	Dry Comb	3.3	4.0	4.0	2.7	4.0	4.0	3.9	2.0	4.2
	Detangle	3.5	4.0	3.7	3.0	4.5	4.5	4.0	2.5	4.3
15	Antistatic	2.5	3.5	3.5	2.3	3.0	3.5	3.0	2.3	3.0
	Bounce/Body	3.5	3.5	3.5	3.0	3.5	3.5	3.2	2.9	3.2
	Manageability	3.0	3.5	3.5	3.0	3.5	3.5	3.2	2.9	3.2
	Shine	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
20										
	Total(Average)	3.15	4.01	3.96	2.84	3.95	4.01	2.86	2.61	3.96

25           These data show that conditioning agents based  
on a combination of compounds having a range of R chain  
lengths have superior performance even though they  
include compounds which used singly exhibit poorer  
conditioning and would thus be expected to detract from  
30 the performance of the combination.

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EXAMPLE 3

This example describes the preparation of conditioner compositions of this invention.

5 Formulation 3-1: Hair Conditioner

<u>Ingredient</u>	<u>Wt. %</u>
Glyceryl Stearate	
Cetyl Alcohol	1.0
Conditioning agent of formula	1.5
10 (1) derived from rapeseed oil acids, X = Cl (71.3% actives)	1.4
DI Water	95.0
Hydroxyethylcellulose -	1.0
"Natrosol 250 HHR CS" (Aqualon)	
Dimethicone Copolyol - Dow Corning 193	0.1
15 Citric Acid (25% aqueous)	to pH 4.5-5.5
Perfume	q.s
Preservative	q.s 100%

Procedure:

- 20 Weigh water into a container. Sprinkle in Natrosol with mixing until there is an even distribution. Weigh glyceryl stearate, cetyl alcohol, and rapeseed conditioning agent into a separate container. Heat the contents of each beaker over a
- 25 steam bath to 70-75°C. Remove water cellulose mixture from bath, attach to agitator, then add in the contents of the other container to the water with mixing. The combination temperature was recorded at 70°C. Allow to cool. At 50°C add premeasured dimethicone copolyol.
- 30 After 24 hours the pH was adjusted with 25% citric acid.

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- 1 Viscosity: Brookfield Viscometer DV2  
Spindle No. 5 at 10 rpm.  
8,000 cps.

The product was a creamy, thick, white liquid  
5 at room temperature and retained this condition, without  
breaking, upon heating to 48°C and after 3 freeze/thaw  
cycles. As a hair conditioner it provides excellent  
feel and detangling benefits.

10 Formulation 3-2: Hair Conditioner

<u>Ingredient</u>	<u>Wt. %</u>
DI Water	90.7
Cetyl Alcohol	3.0
Stearyl Alcohol	0.5
15 Conditioning agent of formula (1) derived from rapeseed oil acids, X = Cl (71.3% actives)	2.8
Ceteareth-20	0.4
Stearamidopropyl Dimethylamine	0.3
DI Water	2.0
Hydrolyzed Protein - "Crotein 20 SPC" (Croda)	0.3
Citric Acid (25% aqueous)	to pH 4.5-5.5
Perfume	q.s
Preservative	<u>q.s</u> 100%

25 Observations & Data:

The water was weighed into a container. The  
other ingredients other than water and citric acid were  
weighed into a separate container. The contents of each  
container were heated over a steam bath to 70-75°C. The  
30 water was removed from the steam bath and attached to a  
mixer, and the second container contents were added with  
agitation. The mixture was allowed to cool with mixing.

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1 At 30°C premixed water and hydrolyzed protein were added. After set-up the pH was adjusted with citric acid.

5 Viscosity: Brookfield DV2 Viscometer.  
Spindle No. 5 at 10 rpm.  
2,520 cps.

The product was a thin, creamy, white liquid and retained this condition, without breaking, upon heating at 48°C and after 3 freeze/thaw cycles. It is a deep conditioning hair conditioner with exceptional afterfeel.

Formulation 3-3: Skin Lotion

	<u>Amt. (gr.)</u>
15 Glyceryl Stearate	4.0
"Protol" (Mineral Oil) (Witco Corp.)	2.0
Cetyl Alcohol	1.0
PEG-8 Stearate	1.0
Conditioning agent of formula	1.3
(1) derived from rapeseed oil	
20 acids, X = Cl, 71.3% actives	
Dow Corning fluid 200 250 CS (Dow Chemical)	0.4
DI Water	86.3
Glycerine	4.0
Lactic Acid	
pH = 3.9	pH 4.5 - 5.0

25 Viscosity: Brookfield DV2 Viscometer.  
Spindle No. 4 at 20 rpm.  
78,000 cps.

30 The product appeared to be a water-in-oil emulsion and imparted a silky feeling to the skin.

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1 Formulation 3-4: Skin Lotion

	<u>Amt. (gr.)</u>
PPG-3 Myristyl ether	6.0
Glyceryl stearate	3.5
Conditioning agent of formula	1.3
5 (1) derived from rapeseed oil acids, X = Cl	
PEG-8 Stearate	1.0
Cetyl Alcohol	0.5
Petrolatum	1.0
Glycerine	4.0
Lactic Acid	0.05
10 DI Water	82.65

Viscosity: Brookfield DV2 Viscometer.

Spindle No. 4 at 20 rpm.

3,200 cps.

15

This product is an oil-in-water emulsion with  
good after-dry feel.

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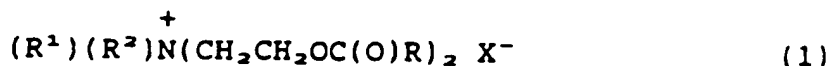
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1 WHAT IS CLAIMED IS:

1. A method for conditioning hair comprising applying to the hair a conditioning effective amount of a composition comprising

- 5 (a) from 0.1 wt.% to 10 wt.% of a mixture of compounds of the formula (1)



wherein  $R^1$  is alkyl containing 1 to 6 carbon atoms, or  
10 hydroxyalkyl containing 1 to 6 carbon atoms;  $R^2$  is alkyl containing 1 to 6 carbon atoms, or benzyl;  $X^-$  is an anion; and R is selected from the group consisting of alkyl and alkylene groups containing 11 to 23 carbon atoms and up to 3 carbon-carbon double bonds, provided  
15 that said mixture contains compounds of formula (1) containing R groups which have at least 2 different chain lengths and containing R groups which have 0, 1 and 2 carbon-carbon double bonds; and

(b) a cosmetically acceptable vehicle which  
20 imparts to said composition fluidity upon application thereof to the hair and which has a pH value compatible with said hair.

2. A method according to Claim 1 wherein the pH value of said composition is about 3.5 to about 5.5.

25 3. A method according to Claim 1 wherein said composition is a solution.

4. A method according to Claim 1 wherein said composition is a water-in-oil emulsion.

30 5. A method according to Claim 1 wherein said composition is an oil-in-water emulsion.

1           6. A method according to Claim 1 wherein the  
structures of the R groups and the amounts thereof are  
those of tallow.

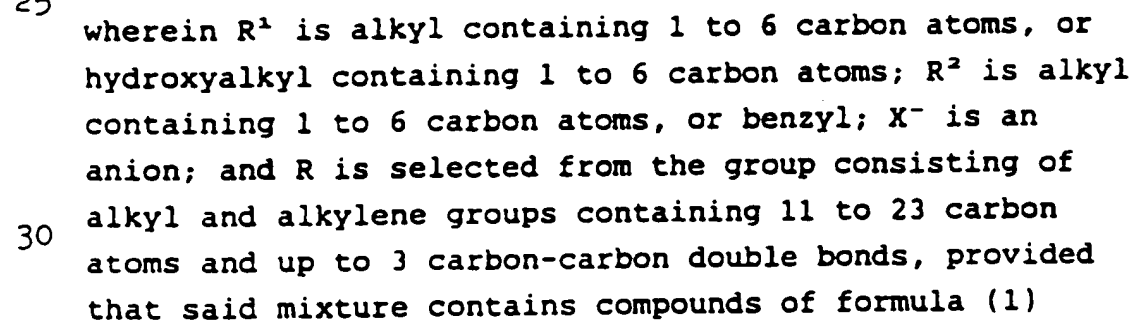
8. A method according to Claim 1 wherein the structures of the R groups and the amounts thereof are those of palm oil.

10. A method according to Claim 1 wherein the structures of the R groups and the amounts thereof are those of rapeseed oil.

11. A method according to Claim 1 wherein X<sup>-</sup> is selected from the group consisting of chloride, bromide, methylsulfate and ethylsulfate.

12. A method for conditioning skin comprising  
20 applying to the skin a conditioning effective amount of  
a composition comprising

(a) from 0.1 wt.% to 10 wt.% of a mixture of compounds of the formula (1)





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1 containing R groups which have at least 2 different  
chain lengths and containing R groups which have 0, 1  
and 2 carbon-carbon double bonds; and

(b) a cosmetically acceptable vehicle which  
5 imparts to said composition fluidity upon application  
thereof to the skin and which has a pH value compatible  
with said skin.

13. A method according to Claim 12 wherein  
the pH value of said composition is about 4.0 to about  
10 5.5.

14. A method according to Claim 12 wherein  
said composition is a solution.

15. A method according to Claim 12 wherein  
said composition is a water-in-oil emulsion.

16. A method according to Claim 12 wherein  
said composition is an oil-in-water emulsion.

17. A method according to Claim 12 wherein  
the structures of the R groups and the amounts thereof  
are those of tallow.

18. A method according to Claim 12 wherein  
the structures of the R groups and the amounts thereof  
are those of rapeseed oil.

19. A method according to Claim 12 wherein  
the structures of the R groups and the amounts thereof  
25 are those of palm stearine.

20. A method according to Claim 12 wherein  
the structures of the R groups and the amounts thereof  
are those of palm oil.

21. A method according to Claim 12 wherein  
30 the structures of the R groups and the amounts thereof  
are those of canola oil.

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1                    22. A method according to Claim 12 wherein X<sup>-</sup>  
is selected from the group consisting of chloride,  
bromide, methylsulfate and ethylsulfate.

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## INTERNATIONAL SEARCH REPORT

International application No

PCT/US95/09960

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : A61K 7/06, A61K 47/00

US CL : 424/070; 514/788, 514/847

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 424/070, 514/847

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
NONEElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
NONE

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 4,978,526 (GESSLEIN ET AL) 18 December 1990, column 2, lines 1-37.	12-22
X	WO, A, 91/17975 (BEROL NOBEL AB) 28 NOVEMBER 1991, see whole document, especially pages 8 and 9.	1-11
X	Ash et al, "A FORMULARY OF COSMETIC PREPARATIONS", published 27 July 1981 by Chemical Publishing Co. (New York), pages 119-129.	1-11

☐ Further documents are listed in the continuation of Box C☐ See patent family annex.

* Special categories of cited documents.	* T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention.	
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* P	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

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Name and mailing address of the ISA/US  
Commissioner of Patents and Trademarks  
Box PCT  
Washington, D.C. 20231

Authorized officer

DALE R. ORB

Facsimile No. (703) 305-3592

Telephone No. (703) 308-1235

